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(54) POLYMERIC BLENDS

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POLYMERIC BLENDS

This invention relates to polymeric blends and more particularly to polymeric blends of polyvinylcyclohexanes and vinylcyclohexane--alkyl-substituted polyethylene block copolymers in which block sequences of poly(vinylcyclohexanes) are covalently bound to block sequences of an alkyl-substituted polyethylene.

Homopolymers of vinylcyclohexane have been known in the art for many years, but have not demonstrated commercial value due to their relatively brittle nature. These polymers have been characterized as clear, rigid, plastics having high heat distortion temperatures but relatively poor impact strengths. Those efforts made to blend rubbery materials with the homopolymers of vinylcyclohexane to improve their impact strength, did not meet with any measure of success and the resulting blends were cloudy, opaque materials with relatively poor impact resistance. Perhaps the primary reason that the homopolymers of vinylcyclohexane were difficult to blend was due to their incompatibility with conventional rubber-like materials.

Block polymers of vinylcyclohexane--alkyl--substituted polyethylene have also been prepared. For example, see our copending application, Serial No. 968,533 on "BLOCK POLYMERS".

It has now been discovered that while vinylcyclohexane polymers are incompatible with conventional rubber-like materials, such as polybutadiene and poly(butadiene-styrene) and the like, these polymers are compatible with the vinyl cyclohexane--alkyl-substituted polyethylene block copolymers described in copending application 968,533 , to the extent that tough, strong, transparent, high heat distortion thermoplastic blends may be prepared.

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The present invention is directed to blends of from about 10 to about 90 parts by weight polyvinylcyclohexane and correspondingly from about 90 to about 10 parts by weight vinylcyclohexane--alkyl-substituted polyethylene block polymers. The blending of these polymers results in polymeric blends having improved impact strengths over those of the polyvinylcyclohexane homopolymers.

The recurring polyvinylcyclohexane portion of the blends of this invention may be represented by the formula:

$$\left[- \underset{R_1}{\overset{R_2}{\overset{|}{\underset{|}{C}}}} - CH_2 - \right]_q$$

FORMULA I

wherein R_1 is a cyclohexyl or substituted cyclohexyl group and R_2 is hydrogen or an alkyl group and q is at least 25.

The vinylcyclohexane--alkyl-substituted polyethylene block copolymers which are blended with the polyvinylcyclohexane polymers contain vinylcyclohexane structural units in linear polymeric block sequences of the formula:

$$\left[- \underset{R_3}{\overset{R_4}{\overset{|}{\underset{|}{C}}}} - CH_2 - \right]_x$$

FORMULA II

wherein R_3 is a cyclohexyl or substituted cyclohexyl group, and R_4 is hydrogen or an alkyl group and x is a whole number between 1 and 25,000 covalently linked to linear polymeric block segments of an alkyl-substituted polyethylene of the formula:

$$\left[- CH_2 - CH_2 - \right]_y \left[- CH_2 - \underset{R_6}{\overset{R_5}{\overset{|}{\underset{|}{C}}}} - \right]_z$$

FORMULA III

wherein R_5 may be hydrogen or a methyl group and R_6 is a hydrogen, methyl, ethyl or isopropyl group, and y and z are whole numbers between 1 and 25,000 in the ratio y/z between 25/1 and 1/100 such that $y + z \leq 25{,}000$. In the block copolymers utilized in the blends of this invention, at least one of x and (y + z) are equal to or greater than 25.

In a preferred embodiment of this invention, in Formulae I and II above, R_1 and R_3 are cyclohexyl groups, and R_2 and R_4 are hydrogen, and Formula III above, R_5 is hydrogen and R_6 is a pendant ethyl group or a pendant methyl group.

The polyvinylcyclohexane polymers utilized in preparing the blends of the present invention are conveniently prepared by the hydrogenation of vinyl-substituted aromatic hydrocarbon polymers such as polymeric styrene, a-methylstyrene, a,o-dimethylstyrene, vinyl toluene, a,m-dimethylstyrene, a,p-dimethylstyrene, o-chlorostyrene, m-chlorostyrene, p-chlorostyrene, vinyl anisole, vinyl naphthalene, vinyl biphenyl, vinyl xylene, o, m, or p-flurorstyrene, vinyl pyridine, and copolymers and mixtures thereof. The aforementioned polymer or copolymer may be conveniently prepared by conventional methods well known to those skilled in the art.

The block copolymers blended with the polyvinylcyclohexane polymers to provide the blends of the present invention are conveniently prepared by the hydrogenation of vinyl-substituted aromatic hydrocarbon-conjugated diene block copolymers. The preferred unsaturated block copolymer substrates utilized in

preparing the block copolymers used in this invention include linear, soluble, gel-free, block copolymers of vinyl aromatic hydrocarbon monomers such as styrene, a-methylstyrene, a,o-dimethylstyrene, vinyl toluene, a,m-dimethylstyrene, a,p-dimethylstyrene, vinyl anisole, vinyl naphthalene, vinyl biphenyl, vinyl xylene, o-chlorostyrene, m-chlorostyrene, p-chlorostyrene, o, m, or p-fluorostyrene, and vinyl pyridine polymerized with a conjugated diene such as butadiene, isoprene, dimethyl butadiene, 1,3-pentadiene or the like. Unsaturated block copolymer substrates of mixtures of the aforementioned monomers may also be utilized.

The unsaturated block copolymer substrates utilized to prepare the block polymers used in this invention may be prepared by a variety of methods such as by using alkali metals or organolithium compounds as polymerization initiators to cause formation of block sequences in a hydrocarbon solution. It will be noted that a variety of different block structures may be obtained by varying the monomer addition sequences, rate of addition, temperature and solvent. For example, mixed block copolymers may be prepared, i.e., SB^{M}, pure block copolymers, i.e., SB, ternary pure block copolymers, i.e., SBS or BSB, from styrene and butadiene monomers. A great variety of unsaturated block polymers used to prepare the block polymers suitable for use in the blends of this invention are set forth in our copending application Serial No. 968,533.

The hydrogenation of the monovinyl aromatic hydrocarbon polymers as well as the unsaturated block copolymers to prepare the blends of this invention may be carried out by a variety of methods. The hydrogenation may be accomplished, for example, by placing the vinyl aromatic hydrocarbon polymer and/or block copolymer substrate in a hydrocarbon solution in the presence of a suitable catalyst and applying hydrogen gas under pressure to this solution.

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The polymer concentration may vary between about 0.5 per cent to about 30 per cent by weight of the hydrocarbon solution and preferably falls within a range of about 2 per cent to about 20 per cent.

Catalysts such as finely divided, supported and unsupported nickel, for example, nickel-on-kieselguhr, have been found to be very effective. The quantity of catalyst may be varied within a range of from about 0.1 to about 400 per cent by weight of the polymer used. In commercial applications, it is desireable to keep down the residence time of the hydrogenation and may be achieved by high catalyst to polymer ratios. When the catalyst is used in high concentrations with respect to the polymer, it must, of course, be separable from the fully hydrogenated product for re-use as a catalyst.

Under certain reaction conditions, for example, above 225° C., it may be desirable to reduce the time in which the catalyst and polymer are in contact, which will also require a high catalyst/polymer ratio.

The hydrogen pressure utilized in hydrogenating these polymers is generally in the range of from about 100 psi to about 5,000 psi and preferably within a range of between about 250 and 3,000 psi.

The temperature of the hydrogenation reaction may range from about 100° C. up to the degradation temperature of the specific polymer being hydrogenated. The temperature range is preferably between about 100° C. and about 350° C.

The reaction time under which these polymers are hydrogenated depends upon the conditions of the reaction and may vary between a few minutes and about 20 hours.

The following examples illustrate the blending of polyvinylcyclohexane polymers and copolymers with vinylcyclohexane--alkyl-substituted polyethylene block copolymers. As indicated in the examples, the copolymer is compatible with the polyvinylcyclohexane polymers within a range of from about 10 per cent by weight block copolymer blended with about 90 per cent by weight polyvinylcyclohexane and correspondingly from about 90 per cent by weight block polymer blended with about 10 per cent by weight polyvinylcyclohexane. Also, it will be noted from Table I that the block copolymer must contain in excess of 10 per cent by weight of vinylcyclohexane structural units to be compatible with the polyvinylcyclohexane.

In the examples, the block copolymers were either first prepared and mechanically blended or blended while in solution with the polyvinylcyclohexane. Alternatively, the blending may be carried out before or during the hydrogenation. The mixed block copolymers of styrene-butadiene are referred to as SB^M. In the tables below, Examples 1 through 4 indicate that blends containing 75 per cent by weight polyvinylcyclohexane and 25 per cent by weight mixed block polymer therein, are compatible and transparent when there is in excess of 10 per cent polyvinylcyclohexane in the block copolymer portion of the blend.

TABLE I

Blends of 75 per cent by weight polyvinylcyclohexane and 25 per cent by weight mixed block polymers

Example No.	Polymer	Wt.% PVCH in Copolymer	Result of Blend with Polyvinylcyclohexane
1	SB^M	10	Incompatible, opaque
2	SB^M	15	Compatible, Transparent
3	SB^M	20	Compatible, Transparent
4	SB^M	70	Compatible, Transparent

Examples 5 through 11 provide the physical properties of polyvinylcyclohexane-block copolymer blends wherein the block copolymer contains 25 per cent by weight vinylcyclohexane structural units.

TABLE II

	Parts by weight of Components of Blend		Physical Properties of Blend		
Ex. No.	SB^{M} Copolymers Containing 25% by weight polyvinylcyclohexane	% by weight polyvinylcyclohexane	Impact Strength Notched Izod ft. lbs.	HDT, °C.	Flexural Modulus psi
5	10	90*	<0.1	117	360,000
6	15	85	---	---	---
7	25	75	0.3	126	210,000
8	30	70	0.9	127	120,000
9	35	65	1.6	120	90,000
10	40	60	3.7	108	71,000
11	50	50	10.0	96	40,000

* Opaque, brittle molding. All the rest were transparent. These were all prepared via solution blending.

Examples 12 through 14 provide the physical properties of blends of polyvinylcyclohexane with various block copolymers; these blends contain from about 10 parts by weight polyvinylcyclohexane blended with about 90 parts by weight block copolymer and correspondingly from about 10 parts by weight block copolymer blended with about 90 parts by weight polyvinylcyclohexane.

TABLE III

Ex. No.	Pts. by wt. Block Copolymer	Pts. by wt. PVCH in Block Copolymer	Pts. by wt. PVCH in Blend	Flex. Mod. psi	HDT °C.	Impact kg.-cm/cm^2
12	90	95	10	420,000	133	3.0
13	10	56	90	---	136	2.4
14	90	56	10	90,000	125	Sample would not break in test.

The examples of the invention have described certain specific compositions of polyvinylcyclohexane prepared from the hydrogenation of polystyrene, blended with vinylcyclohexane--polyethylene block copolymers prepared from the hydrogenation of styrene-butadiene block copolymers, however, it will be understood that other vinylcyclohexane polymers and copolymers as well as other block copolymers may be utilized as indicated by the great variety of polymers that may be hydrogenated to obtain the polymers utilized in the blends of this invention.

The specific embodiments in the examples are not meant to limit, but merely to illustrate the invention. The scope of this invention is defined solely by the appended claims which should be construed as broadly as is consistent with the prior art.

WHAT IS CLAIMED IS:

1. A blend of polymeric material selected from the group consisting of polymers and copolymers containing recurring units of the formula:

$$\left[- \underset{R_1}{\overset{R_2}{\underset{|}{\overset{|}{C}}}} - CH_2 - \right]_q$$

wherein R_1 is selected from the group consisting of cyclohexyl and substituted cyclohexyl groups and R_2 is selected from the group consisting of hydrogen and alkyl groups, and wherein q is at least 25 and a vinylcyclohexane—alkyl-substituted polyethylene block copolymer containing vinylcyclohexane structural units in linear sequences of the formula:

$$\left[- \underset{R_3}{\overset{R_4}{\underset{|}{\overset{|}{C}}}} - CH_2 - \right]_x$$

wherein R_3 is selected from the group consisting of cyclohexyl and substituted cyclohexyl groups and R_4 is selected from the group consisting of hydrogen and alkyl groups, covalently linked to linear block sequences of an alkyl-substituted polyethylene of the formula:

$$\left[- CH_2 - CH_2 - \right]_y \left[- CH_2 - \underset{R_6}{\overset{R_5}{\underset{|}{\overset{|}{C}}}} - \right]_z$$

wherein R_5 is selected from the group consisting of hydrogen and methyl and R_6 is selected from the group consisting of hydrogen, methyl, ethyl and isopropyl groups and wherein x, y, and z are whole numbers between 1 and 25,000 and the ratio of y/z is between 25/1 and 1/100 such that $y + z \leq 25{,}000$ and at least one of x and (y + z) are equal to at least 25.

2. A polymeric blend comprising from about 10 parts by weight to about 90 parts by weight of a vinylcyclohexane polymer and correspondingly from about 90 parts by weight to about 10 parts by weight of a vinylcyclohexane--alkyl-substituted polyethylene block copolymer.

3. The blend of Claim 1 wherein said block copolymer contains in excess of 10 parts by weight vinylcyclohexane.

4. The blend of Claim 1 wherein said block copolymer is a mixed block copolymer.

5. The blend of Claim 1 wherein the block copolymer is a pure block copolymer.

6. The blend of Claim 1 wherein polyvinylcyclohexane is prepared by the hydrogenation of polystyrene and the block copolymer is prepared by the hydrogenation of a styrene-butadiene block polymer.

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